10/585906

IAP20 Rec'd PCT/PTO 12 JUL 2006

TUNGSTEN BASED SINTERED COMPACT AND METHOD FOR PRODUCTION THEREOF

TECHNICAL FIELD

The present invention relates to a tungsten-based sintered body and a production method therefor.

The present invention also relates to a product of the tungsten-based sintered body, such as a discharge lamp electrode, a sputtering target, a crucible, a radiation shielding member, a resistance welding electrode, a semiconductor element mounting substrate, a structural member, a switch contact, a member for semiconductor manufacturing equipment, a member for an ion-implantation apparatus or an internal member for a nuclear fusion reactor.

BACKGROUND ART

Typically, a tungsten-based sintered body has been produced by use of a "electric current-aided sintering process" which is designed to apply a high-voltage pulsed current to a rod-shaped tungsten-based powder compact through a pair of electrodes attached, respectively, to opposite ends of the powder compact, so as to sinter the powder compact.

The electric current-aided sintering process has the following four major disadvantages.

The first disadvantage is that the sintered body has an extremely poor flexibility in shape due to the need for sintering the rod-shaped powder compact in a given gas atmosphere while applying a pulsed current to the powder compact through the electrodes connected to the respective ends thereof. Further, a powder compact having a shape other than a simple rod-like shape is generally necessary to be subjected to an additional process after the sintering. This leads to a considerable increase in production cost.

The second disadvantage is that a sufficient density cannot be obtained without an additional process after the sintering. While the sintered compact may be subjected to a forging process, such as a swaging process, to provide enhanced density, the restriction in shape will become more severe. Further, if it is attempted to obtain a relatively large sintered body with a

sufficient density through a plastic working process, such as a forging process, it is necessary to allow the sintered compact before the forging process to have a larger size causing the need for a single-purpose facility requiring a large cost. Moreover, during the forging process in the single-purpose facility, the sintered compact must be processed at high pressure and high temperature because it has a high strength at elevated temperature. This also leads to a large increase in production cost.

The third disadvantage is that a crystal structure of the sintered compact is distorted or deformed due to the forging process. For example, when the sintered compact is subjected to a swaging process, a crystal structure thereof will be anisotropically orientated to cause anisotropy in strength, electric conductivity, thermal conduction, etc. Thus, an obtained sintered body will deteriorate in uniformity.

The fourth disadvantage is that, due to a dislocation introduced in the crystal structure during the forging process, a recrystallization phenomenon occurs in the forged compact when it is heated up to a given temperature or more. The recrystallization is likely to cause a significant change in properties of a sintered body to be obtained, and adversely affect an intended performance thereof.

With a view to solve the above disadvantages, the following Patent Publication 1 discloses a method for producing a tungsten-based sintered article without using the electric current-aided sintering process. This method comprises pressing a tungsten-based powder to form a powder compact, degreasing and sintering the powder compact to form a sintered compact (i.e. subjecting the tungsten-based powder to a process which is commonly used in ceramics and hard metals), and then subjecting the sintered compact to a hot isostatic press (HIP) process. More specifically, in this technique, a tungsten-based powder compact pressed at 140 to 310 MPa is sintered in a non-oxidizing atmosphere to form a sintered compact having a density of 17.7 to 18.4 g/cm^3, and then the sintered compact is subjected to an HIP process at 1850°C in an argon gas atmosphere of 1360 to 1940 atm, to produce a final sintered article having a density of 18.9 to 19.2 g/cm^3.

The following Patent Publication 2 discloses a method comprising pressing a tungsten powder at a pressure of 98 to 147 MPa to form a powder compact, sintering the powder compact

in a hydrogen atmosphere at 1600 to 1700°C for a holding time of 10 hours to form a sintered compact having a density of 17.0 to 18.2 g/cm^3, and then subjecting the sintered compact to an HIP process at 1460°C in an argon gas atmosphere of 1800 atm.

For example, an upper limit on the density of the tungsten-based or tungsten sintered body to be obtained by the production methods disclosed in the Patent Publications 1 and 2 is 19.16 g/cm^3 which is 99.3% of a theoretical maximum density. This density is not sufficient when the sintered body is used in a large electrode for a light source based on a vacuum system, such as a discharge lamp. Specifically, gas and/or impurities are accumulated in pores of the sintered body, and released therefrom during lighting to cause various negative effects. Thus, it is desirable to minimize the volume of pores as much as possible. In view of preventing adverse effects of the pores, a tungsten-based sintered body should have a porosity of less than 0.5%, or a pure-tungsten sintered body should have a density of 19.25 g/cm^3 or more (a desirable density is varied depending on the type and/or amount of additives).

In addition to the discharge lamp electrode, a target product requiring a low porosity or a high density in a tungsten-based sintered body includes a high-temperature structural member, a radiation shielding member, a resistance welding electrode, a crucible, a sputtering target, a member for semiconductor manufacturing equipment, a semiconductor element mounting substrate, and a switch contact. All of these products can achieve better characteristics as the sintered body has a lower porosity.

[Patent Publication 1] U.S. Patent No. 4,612,162

[Patent Publication 2] Japanese Patent No. 3121400

DISCLOSURE OF THE INVENTION

In view of the above circumstances, it is an object of the present invention to provide a tungsten-based sintered body having a relative density of 99.5% or more (a porosity of 0.5 volume % or less) and a uniform and isotropic structure, which has not been able to be achieved by conventional techniques. Specifically, the sintered body has an average crystal grain size of 30 μm or less, and a composition consisting of at least either one selected from the group consisting of: tungsten; doped tungsten consisting of tungsten doped with 100 ppm or less

(except for zero ppm) of alkali metal; a material consisting of tungsten containing up to 4 weight% (except for zero weight%) of at least one additive selected from the group consisting of oxides of cerium, thorium, lanthanum, yttrium, strontium, calcium, zirconium and hafnium; and a tungsten-molybdenum alloy. It is another object of the present invention to provide a tungsten-based sintered body including pores each having a major axis of 1 μm or more, wherein the number of the pores is 10000 or less per 1 mm^2 of unit cross-sectional area thereof.

In particular, the present invention is intended to provide the following characteristics to the above sintered body.

(1) The sintered body has a hardness difference of 1.0 or less in terms of HRA between a surface portion and an inside portion thereof.

(2) The sintered body has a recrystallization temperature of at least 1600°C or more.

(3) The sintered body has a ratio of a minimum value to a maximum value of an electric resistivity of 1.1 or less between any two points therein.

(4) The sintered body has a ratio of a minimum value to a maximum value of a thermal conductivity of 1.1 or less between any two points therein.

It is yet another object of the present invention to provide a discharge lamp electrode, a sputtering target, a crucible, a radiation shielding member, a resistance welding electrode, a semiconductor element mounting substrate, a structural member, a switch contact, a member for semiconductor manufacturing equipment, a member for an ion-implantation apparatus, and an internal member for a nuclear fusion reactor, which are formed of the above sintered body.

It is still another object of the present invention to provide a method for producing a tungsten-based sintered body which has a relative density of 99.5% or more, an isotropic and uniform structure, and an average crystal grain size of 30 μm or less.

In order to achieve the above objects, as set forth in the appended claim 1, the present invention provides a tungsten-based sintered body consisting of at least either one selected from the group consisting of: tungsten; doped tungsten consisting of tungsten doped with 100 ppm or less (except for zero ppm) of alkali metal or consisting of tungsten containing 4 weight% or less (except for zero weight%) of at least one additive selected from the group consisting of oxides of cerium, thorium, lanthanum, yttrium, strontium, calcium, zirconium and hafnium; and a

tungsten-molybdenum alloy. The tungsten-based sintered body has an isotropic crystal structure, a relative density of 99.5% or more, and an average crystal grain size of 30 μm or less.

The sintered body of the present invention has a relative density of 99.5% or more. This makes it possible to significantly reduce gas and/or impurities mainly intruding into pores of the sintered body so as to eliminate adverse effects thereof in the surrounding atmosphere.

In addition, the sintered body of the present invention has an isotropic structure. Thus, characteristics of the sintered body, such as mechanical characteristics, electrical characteristic and discharge characteristic, are stably kept constant in any direction.

Considering that an excessively large grain size causes significant deterioration in strength, the average crystal grain size of the sintered body is desirably set at 30 μm or less.

In order to provide an enhanced discharge characteristic and a higher recrystallization temperature, and prevent grain growth, the tungsten-based sintered body may contain various additives depending on intended purposes. The additive is selected from 100 ppm or less of alkali metal, and 4 weight% or less of at least one oxide of cerium, thorium, lanthanum, yttrium, strontium, calcium, zirconium, hafnium and molybdenum, depending on intended purposes of the sintered body. In some cases where a specific discharge characteristic is required, or the above additives are unfit for a specific purpose, the sintered body may consist of high-purity tungsten (purity of 99.95 to 99.99999%).

As set forth in the appended claim 2, the tungsten-based sintered body of the present invention may include pores each having a major axis of 1 μm or more, wherein the number of the pores is 10000 or less per 1 mm^2 of unit cross-sectional area thereof.

Even if the sintered body has a relative density of 99.5% or more, it can be unfit for use in some purposes depending on configuration and/or distribution of pores therein. For example, if the sintered body includes pores having a diameter of greater than 5 μm, such pores are likely to cause deformation during use at high temperatures, and increase in gas residing therein. As to the distribution of pores, it is preferable that pores each having a diameter of 1 μm or less are evenly distributed. It is preferable to minimize the number of pores each having a diameter of greater than 1 μm, as much as possible. Specifically, the number of the pores may be set to be 10000 or less per 1 mm^2 of unit cross-sectional area of the sintered body to sufficiently satisfy

this requirement. Further, if these pores are located adjacent to a grain boundary, they will be easily moved to the grain boundary and vanished. Thus, more preferably, the pores are formed such that at least one-half of the entire volume thereof resides within crystal grains. This makes it difficult for the pores to be moved to grain boundaries and vanished in use environments so as to prevent gas in the pores from being released outside the sintered body.

As set forth in the appended claim 3, the above tungsten-based sintered body may have a hardness difference of 1.0 or less in terms of HRA between a surface portion and an inside portion thereof. A hardness difference between a surface portion and an inside portion of a sintered body causes not only deterioration in workability when the sintered body is fabricated in a final product, but also adverse effects on of finish surface roughness, and mechanical characteristics, such as wear resistance, as a structural member.

An allowable hardness difference for avoiding such negative effects is 1.0 or less in terms of HRA.

As set forth in the appended claim 4, the above tungsten-based sintered body may have a recrystallization temperature of at least 1600°C or more. A recrystallization phenomenon occurs at a lower temperature (1300 to 1500°C) when a sintered compact is subjected to a plastic working process, such as a forging process. The tungsten-based sintered body is produced without a plastic working process, such as a forging process, and therefore the recrystallization temperature thereof is significantly high. In a sintered body having a recrystallization temperature of less than 1600°C, a slip occurs at grain boundaries, particularly, in a thin portion thereof, to cause deformation therein. Thus, when the tungsten-based sintered body is used for forming a structural member or an electrode to be used, particularly, in high-temperature atmosphere, it is more preferable to have a higher recrystallization temperature of 2000°C or more.

As set forth in the appended claim 5, the above tungsten-based sintered body may have a ratio of a minimum value to a maximum value of an electric resistivity of 1.1 or less between any two points therein.

When the tungsten-based sintered body is used for a resistance welding electrode or a switch contact, an electric resistivity of the sintered body becomes a key factor in design. If an

electric resistivity largely varies between any two points in the sintered body, a current flow, heat generation during switching, an arc resistance and ablation/wearing will become unstable to cause the need for setting a wider tolerance. The sintered body of the present invention has an approximately constant electric resistivity in any direction thereof, and the ratio of a minimum value to a maximum value of the electric resistivity is 1.1 or less. Thus, the sintered body of the present invention can be used in a resistance welding electrode or a switch contact without any regard for a crystal orientation thereof.

As set forth in the appended claim 6, the above tungsten-based sintered body may have a ratio of a minimum value to a maximum value of a thermal conductivity of 1.1 or less between any two points therein.

When the tungsten-based sintered body is used for a heat-radiation member or a semiconductor element mounting substrate, a thermal conductivity of the sintered body becomes a key factor. If a thermal conductivity largely varies between any two points in the sintered body, a heat radiation rate and a temperature gradient will become unstable to impose severe restrictions on design. The sintered body of the present invention has an approximately constant thermal conductivity in any direction thereof, and the ratio of a minimum value to a maximum value of the thermal conductivity is 1.1 or less. Thus, the sintered body of the present invention can be used in a heat-radiation member or a semiconductor element mounting substrate without any regard for a crystal orientation thereof.

As set forth in the appended claim 7, the present invention provides a discharge lamp electrode formed of the above tungsten-based sintered body. A discharge lamp electrode is required to have various characteristics. Major ones of them are described as follows.

(1) Providing excellent discharge characteristic

(2) Free from causing contamination in a discharge lamp due to impurities therefrom during use

(3) Having a high thermal conductivity sufficient to prevent abnormal heat generation in a discharge lamp

(4) Having no deformation during use even in a thin electrode

The discharge lamp electrode of the present invention formed of the tungsten-based sintered

body can exhibit an excellent discharge characteristic. In this case, the tungsten-based sintered body may be made of a suitable material selected, for example, from high-purity tungsten and tungsten doped with 100 ppm or less of alkali metal, depending on intended purposes and/or filler gases.

During use, most impurities reside in pores of the sintered body in the form of gas. In the discharge lamp electrode of the present invention, the number of pores is significantly small, and the number of pores each having a diameter of greater than 1 μm is also small. Thus, an amount of gas to be generated as a contaminated source is significantly small. In addition, the pores are evenly distributed over the entire sintered body, and therefore a degree of contamination is less susceptible to a shape or configuration of the electrode.

Further, the discharge lamp electrode of the present invention can have an approximately constant electric resistivity in any direction thereof. Thus, an electrical resistivity thereof is less susceptible to a crystal orientation of the sintered body so as to assure enhanced reliability against abnormal heat generation.

Furthermore, the discharge lamp electrode of the present invention can have a high recrystallization temperature to prevent the occurrence of recrystallization during use so as to suppress deformation even in a thin portion thereof.

As set forth in the appended claim 8, the present invention provides a sputtering target formed of the above tungsten-based sintered body. A sputtering target is required to immunize an amount of impurities and a volume or number of pores. If the sputtering target includes a large volume or number of pores, a wearing will occur around the pores during use (this wearing will hereinafter be referred to as "uneven wearing"). The sputtering target of the present invention has a high relative density of 99.5% or more, and therefore causes less uneven wearing. In addition, the sputtering target of the present invention has a small volume or number of pores. Thus, an amount of gas or impurities residing in the pores can be significantly reduced to allow the sputtering target to avoid contamination due to the impurities.

As set forth in the appended claim 9, the present invention provides a crucible formed of the above tungsten-based sintered body. While a tungsten-based sintered body is generally suitable for a crucible to be used in a high-temperature environment, a key point in this application is

contamination due to the crucible.

While a component causing the contamination varies depending on use environments and/or a material to be molted in the crucible, a contamination source mostly arises from gas residing in pores of the crucible and a substance attached on inner walls of the pores.

The crucible of the present invention has a significantly small volume or number of pores. This makes it possible to reduce gas and adherent substance as a contamination source so as to minimize the occurrence of contamination.

As set forth in the appended claim 10, the present invention provides a radiation shielding member formed of the above tungsten-based sintered body. A radiation shielding performance of a radiation shielding member is proportional to a density thereof. The radiation shielding member of the present invention has a density of 19.25 g/cm^3 during use, and therefore exhibits a higher radiation shielding performance than that of a radiation shielding member formed of a conventional tungsten-based sintered body.

As set forth in the appended claim 11, the present invention provides a resistance welding electrode formed of the above tungsten-based sintered body. In some cases, a tip portion of a resistance welding electrode is formed of a tungsten-based sintered body. The electrode tip is required to have various characteristics, such as fusion resistance, thermal resistance and electric resistivity. Among these required characteristics, a desirable thermal shock resistance has not been obtained by the conventional tungsten-based sintered body. In contrast, the resistance welding electrode of the present invention having a small volume or number of pores and an isotropic crystal structure exhibits a high thermal shock resistance in all directions. Thus, the resistance welding electrode of the present invention can suppress the occurrence of cracks or chips due to thermal shock, and the propagation of a crack even if it occurs. This makes it possible to achieve excellent characteristics as a resistance welding electrode.

As set forth in the appended claim 12, the present invention provides a semiconductor element mounting substrate formed of the above tungsten-based sintered body. A semiconductor element mounting substrate is required to have a given thermal expansion coefficient and thermal conductivity. The semiconductor element mounting substrate of the present invention has an isotropic crystal structure and therefore exhibits no anisotropic

characteristic in thermal expansion. In addition, the semiconductor element mounting substrate of the present invention has a small volume or number of pores and therefore exhibits a high thermal conductivity. This allows semiconductor element mounting substrate to efficiently release heat in all directions and exhibit excellent characteristics.

As set forth in the appended claim 13, the present invention provides a structural member formed of the above tungsten-based sintered body.

A structural member is formed in various shapes, such as a block-like shape, a pipe-like shape, a plate-like shape and a rod-like shape, depending on intended purposes.

In particular, a structural member to be used in a high-temperature environment is required to have an adequate strength without the occurrence of environmental contamination during use. As mentioned above, the structural member of the present invention is substantially free from causing contamination of a use environment. In addition, the structural member of the present invention having a high recrystallization temperature can be used without the occurrence of recrystallization. In contrast, a structural member formed of a conventional tungsten-based sintered body having a lower recrystallization temperature is likely to cause recrystallization during use, and significant deterioration in strength at elevated temperature.

As set forth in the appended claim 14, the present invention provides a switch contact formed of the above tungsten-based sintered body. A switch contact is required to have a high melting point and a low electric resistivity. While the semiconductor element mounting substrate of the present invention has a melting point equivalent to that of a switch contact formed of a conventional tungsten-based sintered body, it has a small volume or number of pores and therefore exhibits a higher thermal conductivity which is approximately constant in any direction. Thus, the switch contact of the present invention can effectively release heat in all directions to exhibit excellent characteristics.

As set forth in the appended claim 15, the present invention provides a member for semiconductor manufacturing equipment, which is formed of the above tungsten-based sintered body. Tungsten-based material having a high melting point, no magnetism and a high plasma resistance is suitably used in a member for semiconductor manufacturing equipment. Among them, the tungsten-based sintered body of the present invention having a high purity is

particularly suitable because it exhibits less contamination of semiconductors and surrounding members.

As set forth in the appended claim 16, the present invention provides a member for an ion-implantation apparatus, which is formed of the above tungsten-based sintered body. Among various members for semiconductor manufacturing equipment, a member for an ion-implantation apparatus is exposed to plasma and high temperatures. Thus, a tungsten-based sintered body is suitable as a material of a member for an ion-implantation apparatus, particularly, of an ion source chamber. The tungsten-based sintered body of the present invention having a high purity, a high density and a small volume or number of pores is particularly suitable because it exhibits less contamination of semiconductor wafers and exhibit high plasma resistance.

As set forth in the appended claim 17, the present invention provides an internal member for a nuclear fusion reactor, which is formed of the above tungsten-based sintered body. The internal member of the present invention is made of a tungsten-based material having a high melting point, and therefor less susceptible to fusion in a reactor. In addition, the internal member is excellent in sputtering resistance, and less susceptible to vaporization even in a high temperature environment. Further, as compared with a conventional carbon-based member, the internal member has a lower absorbability of H-3 (tritium), and therefore can reduce radioactive contamination.

As set forth in the appended claim 18, the present invention provides a method for producing a tungsten-based sintered body, which comprises: subjecting a raw powder having an average particle size of 0.5 to 4 μm to a CIP process at a pressure of 350 MPa or more to form a powder compact, wherein the raw material consists of at least either one selected from the group consisting of: tungsten; doped tungsten consisting of tungsten doped with 100 ppm or less of alkali metal; a material consisting of tungsten containing up to 4 weight% of at least one additive selected from the group consisting of oxides of cerium, thorium, lanthanum, yttrium, strontium, calcium, zirconium and hafnium; and a tungsten-molybdenum alloy; sintering the powder compact in a hydrogen gas atmosphere at a sintering temperature of 1600°C or more for a holding time of 5 hours or more to form a sintered compact; and subjecting the sintered compact to a HIP process in an argon gas atmosphere under conditions of 150 MPa or more and 1900°C

or more.

The tungsten-based sintered body production method of the present invention has the following features 1 to 6.

1. The method includes at least compacting of the raw powder based on a CIP process; sintering; and a HIP process.

2. The raw material consists of at least either one selected from the group consisting of: tungsten; doped tungsten consisting of tungsten doped with 100 ppm or less of alkali metal; a material consisting of tungsten containing up to 4 weight% of at least one additive selected from the group consisting of oxides of cerium, thorium, lanthanum, yttrium, strontium, calcium, zirconium and hafnium; and a tungsten-molybdenum alloy.

3. The raw powder has an average particle size of 0.5 to 4 μm.

4. The CIP process for the raw powder is performed at a pressure of 350 MPa.

5. The sintering process is performed in a hydrogen gas atmosphere at a sintering temperature of 1600°C or more for a holding time of 5 hours or more.

6. The HIP process is performed in an argon gas atmosphere under conditions of 150 MPa or more and 1900°C or more.

The above features 3 to 6 will be more specifically described below.

[Feature 3: the raw powder has an average particle size of 0.5 to 4 μm]

The average particle size is set to be 0.5 μm or more, because it is difficult to industrially produce a tungsten powder having an average particle size of less than 0.5 μm, and, even if it can be produced by intensive grinding or the like, an obtained powder is hardly handled due to its high active or susceptibility to oxidization. Further, the average particle size is set to be 4 μm or less, because a powder having an average particle size of greater than 4 μm causes deterioration in degree of sintering during sintering.

[Feature 4: the CIP process for the raw powder is performed at a pressure of 350 MPa]

Pressures during the CIP process (CIP pressures) disclosed in the Patent Publication 1 and the Patent Publication 2 are set in the range of 140 to 310 MPa and in the range of 100 to 150 MPa, respectively. If a CIP pressure is set in these ranges, a tungsten powder having an average particle size of 0.5 to 4 μm cannot be sufficiently crushed. FIG. 1 shows a relationship

between a CIP pressure for a powder of 1 μm and a density of a tungsten-based sintered compact just after a sintering process. The sintering process was performed in a hydrogen gas atmosphere at a temperature of 1700°C for a holding time of 10 hours.

As is evidenced from the result in FIG. 1, the CIP pressure is required to be 350 MPa at minimum. A sintered compact having an adequate density cannot be obtained at a CIP pressure of 310 MPa or less, even if the sintering temperature is increased.

Sintered compacts obtained by the sintering processes disclosed in the Patent Publications 1 and 2 had insufficient densities of 17.7 to 18.4 g/cm^3 and about 17 g/cm^3, respectively (Patent Publications 1 and 2 include no specific description). When the CIP pressure is set at 350 MPa or more as defined in the present invention, a sintered compact just after the sintering process can have a density of 18.7 g/cm^3 or more.

[Feature 5: the sintering process is performed in a hydrogen gas atmosphere at a sintering temperature of 1600°C or more for a holding time of 5 hours or more]

A sintering atmosphere must be a hydrogen gas atmosphere. Among reduction atmospheres, the hydrogen gas atmosphere exhibits less contamination to tungsten and has an additional function of reacting with impurities in the tungsten at a high temperature to eliminate them. A vacuum atmosphere or an inert gas atmosphere, such as an argon gas atmosphere, cannot sufficiently eliminate such impurities, and a carbon reduction atmosphere causes contamination due to carbon.

A desirable sintering temperature is 1600°C or more, and a desirable holding time is 5 hours or more. FIG. 2 shows a result obtained by subjecting a powder having an average particle size of 1 μm to a CIP process at 400 MPa to form a plurality of compact samples, sintering the respective samples in a hydrogen gas atmosphere while changing a sintering temperature and a holding time to form a plurality of sintered samples, and measuring each density of the sintered samples.

This result shows that a density of 18.6 g/cm^3 or more, i.e. a density required for a sintered compact before the HIP process, can be obtained only if the sintering process is performed at a sintering temperature of 1600°C or more for a holding time of 5 hours or more.

[Feature 6: the HIP process is performed in an argon gas atmosphere under conditions of

150 MPa or more and 1900°C or more]

The Patent Publications 1 and 2 disclose a HIP process performed in an argon gas atmosphere under conditions of 200 MPa and 1850°C at a maximum. In these HIP conditions, while the pressure is satisfactory, the temperature is hardly adequate. Table 1 shows a result obtained by preparing a plurality of samples sintered to have a density of 18.7 g/cm^3, and subjecting the respective samples to a HIP process while changing HIP conditions.

Table 1

Atmosphere	Pressure (MPa)	Temperature (°C)	Density after HIP Process (g/cm^3)
Ar	100	1900	19.20
Ar	150	1900	19.26
Ar	200	1900	19.28
Ar	100	1850	19.17
Ar	150	1850	19.14
Ar	200	1850	19.10
N_2	200	1900	19.15
H_2	200	1900	19.18

Sample: tungsten having a density after sintering of 18.7 g/cm^3

This result shows that a density of 19.25 g/cm^3 or more, i.e. a desirable density of a sintered body after a HIP process, can be obtained only if the HIP process is performed in an argon gas atmosphere under conditions of 150 MPa or more and 1900°C or more.

Table 2 shows a result obtained by subjecting a plurality of sintered compacts having a density of 18.3 to 19.0 g/cm^3 to a HIP process in an argon gas atmosphere under conditions of 150 MPa and 1900°C, and measuring each density of resulting sintered bodies. This result also shows that a sintered compact after the sintering process is required to have a density of 18.6 g/cm^3 or more.

Table 2

Density before HIP Process (g/cm^3)	Density after HIP Process (g/cm^3)
18.2	19.10
18.5	19.17
18.6	19.25
18.7	19.27
18.9	19.28
19.0	19.30

To sum the above results up, the following facts can be pointed out.

1. A density of 99.5% (19.25 g/cm^3) or more, i.e. a density required for a sintered body after a HIP process, can be obtained only if the HIP process is performed in an argon gas atmosphere under conditions of 150 MPa or more and 1900°C or more.

2. The density after the HIP process of 19.25 g/cm^3 or more can be obtained only if a sintered compact has a density of at least 18.6 g/cm^3 or more just after a sintering process.

3. The sintered compact having a density of 18.6 g/cm^3 or more just after a sintering process can be obtained only if the sintering process is performed in a hydrogen atmosphere at a sintering temperature of 1600°C or more for a holding time of 5 hours or more.

4. A powder compact for allowing the sintered compact to have a density of 18.6 g/cm^3 or more just after the sintering process can be obtained only if a CIP process is performed at a pressure of 350 MPa or more.

That is, a tungsten-based sintered body having a relative density of 99.5% can be obtained without any plastic working process, such as a forging process, only if its production process is performed in a manner satisfying all of the above conditions.

As above, the tungsten-based sintered body of the present invention is a high-density homogeneous tungsten-based sintered body which has a small volume or number of pores, a high recrystallization temperature, an isotropic characteristic in hardness, thermal conductivity or thermal expansion coefficient, and a significantly small difference in hardness, thermal conductivity or thermal expansion coefficient between a surface portion and an inside portion thereof.

By taking advantage of these characteristics, the tungsten-based sintered body of the present invention is suitable, particularly, for a discharge lamp electrode, a sputtering target, a crucible, a radiation shielding member, a semiconductor element mounting substrate, a structural member, and a switch contact, to bring about effects of providing enhanced efficiency, enhanced durability, enhanced stability in electric characteristics, and enhanced strength at elevated temperature, while suppressing the generation of contamination and preventing uneven wearing or abrasion.

The tungsten-based sintered body production method of the present invention has the

following effects.

1. As compared with the method disclosed in the Patent Publication 1, the production method of the present invention makes it possible to provide a sintered body after the HIP process at a higher density of 99.5% or more relative to a theoretical density.

2. As compared with the conventional tungsten-based sintered body production method based on a electric current-aided sintering process and a forging process, the production method of the present invention makes it possible to provide increased flexibility in shape of a sintered body. Further, the production method of the present invention has no need for increasing density based on deformation in a forging process. Thus, the production method of the present invention is suitable for production of a large member which is difficult to be subjected to a forging process. In addition, such a large member can be produced at a relatively low cost.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing a relationship between a pressure during a CIP process and a density of a sintered compact.

FIG. 2 is a graph showing a relationship between a sintering time/temperature and a density of a sintered body.

BEST MODE FOR CARRYING OUT THE INVENTION

A preferred embodiment of the present invention will now be described.

In order to obtain an intended sintered body, a raw material is prepared.

Depending on intended purposes, a raw powder is selected from the group consisting of: tungsten; doped tungsten consisting of tungsten doped with 100 ppm or less of alkali metal; a material consisting of tungsten containing up to 4 weight% of at least one additive selected from the group consisting of oxides of cerium, thorium, lanthanum, yttrium, strontium, calcium, zirconium and hafnium; and a tungsten-molybdenum alloy. In a specific application, the above tungsten may be high-purity tungsten (purity of 99.95 to 99.99999%).

The raw powder is prepared to have an average particle size of 0.5 to 4 μm. During preparation of the powder, an organic bonder may be added thereto. An addition of a suitable

organic binder provides enhanced compacting during a CIP process and makes it easy to subsequently add an intermediate working or machining. The added organic binder will be removed or debindered during a sintering process.

Then, the powder is subjected to a CIP process. The CIP process is performed within a closed vessel made of flexible rubber or resin. The powder may be put in the vessel, or may be preformed, for example, through die pressing, and then subjected to the CIP process. Further, the CIP process may be performed two times in different pressures.

The CIP process may be performed in a liquid contained in the vessel to serve as a pressure medium. Alternatively, a dry-type CIP machine (rubber press machine) may be used.

An essential condition for the CIP process is to apply a pressure of 350 MPa or more at least once. After the CIP process, an obtained powder compact is subjected to an intermediate working or machining if needed, and subjected to a sintering process. The intermediate working/machining performed to the powder compact has an overwhelming advantage in process cost and time as compared with working/machining performed to a sintered compact or body.

A furnace for the sintering process is required to have a performance capable of performing the sintering process in a hydrogen gas atmosphere and heating the powder compact up to 1600°C or more.

A heating rate during the sintering process is not limited to a specific value, but a heating to 1000°C may be performed at a higher heating rate to avoid a particular negative effect on a sintered compact to be obtained. A heating rate from 1000°C to a sintering temperature is preferably set in the range of 1 to 30°C/min, depending on a size of the sintered compact. A cooling rate after sintering is set in the same manner. After cooling, a sintered compact can be obtained.

The obtained sintered compact is subjected to a HIP process. While the HIP process may be performed using a conventional HIP apparatus, the HIP apparatus is required to have a performance capable of performing the HIP process in an argon gas atmosphere under conditions of 150 MPa and 1900°C, at lowest. A heating rate or a high-temperature holding time may be set in the usual manner.

After the HIP process, an obtained sintered body is subjected to mechanical and/or electric workings according to need, to obtain the intended tungsten-based sintered body of the present invention.

The obtained tungsten-based sintered body has the following characteristics by changing the particle size of the raw powder and/or the production conditions (sintering conditions, HIP conditions, etc.) in the aforementioned ranges.

(1) The number of pores each having a major axis of 1 μm or more is 10000 or less per 1 mm^2 of unit cross-sectional area of the sintered body.

(2) A hardness difference between a surface portion and an inside portion of the sintered body is 1.0 or less in terms of HRA.

(3) A recrystallization temperature of the sintered body is at least 1600°C or more.

(4) A ratio of a minimum value to a maximum value of an electric resistivity between any two points in the sintered body is 1.1 or less.

(5) A ratio of a minimum value to a maximum value of a thermal conductivity between any two points in the sintered body is 1.1 or less.

Further, the obtained tungsten-based sintered body can be changed in shape to obtain each of a discharge lamp electrode, a sputtering target, a crucible, a radiation shielding member, a resistance welding electrode, a semiconductor element mounting substrate, a structural member, a switch contact, a member for semiconductor manufacturing equipment, a member for an ion-implantation apparatus, and an internal member for a nuclear fusion reactor (as set forth in the appended claims 7 to 17).

The present invention will be more specifically described based on the following Examples.

[EXAMPLE 1]

Example 1 is one example of a discharge lamp electrode formed of the tungsten-based sintered body of the present invention.

A tungsten powder having a purity of 99.99% and an average particle size of 0.8 μ was used as a starting material.

The powder was subjected to die pressing at a pressure of 2 MPa to form a cylindrical-shaped preform of φ 100 × 250. This preform was put in a hermetically-closable

rubber bag and subjected to a CIP process at a pressure of 400 MPa.

A powder compact after the CIP process had a size of φ 80 × 200 and a density of about 11 g/cm^3.

This powder compact was formed in a discharge-lamp-electrode shape having a cylindrical column with a hemispherical head, using a lathe.

The machined powder compact was sintered in a hydrogen gas atmosphere at a temperature of 1800°C for a holding time of 6 hours. The powder compact was heated to 1000°C at a heating rate of 10°C/min and then heated to 1800°C at a heating rate of 4°C/min.

A sintered compact obtained through the sintering process had a density of 18.8 g/cm^3.

The sintered compact was subjected to a HIP process in an argon gas atmosphere under conditions of 200 MPa and 2000°C. A sintered body obtained through the HIP process has a density of 19.28 g/cm^3 (99.9%) approximately equal to a theoretical density. As a result of microscopic observation, it was verified that the sintered body has an isotropic crystal structure, and an average grain size of 15 μm. In a comparison between a surface portion and an inside portion of the sintered body after the HIP process, no difference in crystal structure was found.

The sintered body after the HIP process was formed in a desired shape using a cylindrical grinding machine and a turning center, to obtain a discharge lamp electrode.

The obtain discharge lamp electrode was used as a positive electrode of a discharge lamp. The discharge lamp has less contamination thereinside, and could maintain a high intensity. The positive electrode exhibited less wearing and enhanced durability.

Table 3 shows differences between this discharge lamp electrode and a conventional discharge lamp electrode.

Table 3

Sample	Production Method	Density (g/cm^3)	Feature	Effect
(Inventive Example) 99.99% tungsten	Production Method of the present invention	19.28	Recrystallization Temperature: high Number of pores: small	Lamp Life: long Large-diameter electrode: low cost Small-diameter electrode: small deformation
(Comparative Example) 99.99% tungsten	CIP: 300 MPa Sintering: 1600°C (H_2) HIP: 1850°C, 1500 atm (Ar)	19.18	Recrystallization Temperature: high Number of pores: large	Lamp Life: short Large-diameter electrode: low cost Small-diameter electrode: small deformation
(Comparative Example) 99.99% tungsten	CIP: 120 MPa Sintering: 1650°C (H_2) HIP: 1460°C, 1800 atm (Ar)	19.10	Recrystallization Temperature: high Number of pores: large	Lamp Life: short Large-diameter electrode: low cost Small-diameter electrode: small deformation
(Comparative Example) 99.99% tungsten	Electric Current-aided Sintering + Forging	19.23	Occurrence of recrystallization during use Number of pores: small	Large-diameter (φ 30 or more) electrode: extremely high cost or production NG Small-diameter electrode: large deformation

[EXAMPLE 2]

In the same manner as Example 1 except for the raw powder and a shape of the sintered body, a sputtering target, a crucible, a radiation shielding member, a resistance welding electrode, a semiconductor element mounting substrate and a switch contact were produced. Table 4 shows their advantages in performance and cost, based on the sintered body of the present invention.

Table 4

Product	Comparative Product	Feature	Advantage
Sputtering Target	Tungsten sputtering target with a density of less than 99.5%	Small number of pores	Prevention of uneven wearing Low contamination
		High purity	Low contamination
		Uniform structure	Prevention of uneven wearing
Crucible	Tungsten crucible with a density of less than 99.5%	Small number of pores	Low contamination
		Intermediate working OK	Low production cost
Radiation Shielding Member	Tungsten shielding plate obtained through a forging process	High density	High shielding effect
		Intermediate working OK	Low production cost
Resistance Welding Electrode (chip)	Tungsten chip for a resistance welding electrode, subjected to a forging process	Small number of pores	High thermal shock resistance
		Isotropic characteristic (electric resistivity)	Constant electric resistance Reduction of uneven welding
		Intermediate working OK	Low production cost
Semiconductor Element Mounting Substrate	Semiconductor element mounting tungsten substrate with a density of less than 99.5%	High thermal conductivity	High heat release performance
		Isotropic characteristic (thermal conductivity)	Constant heat release characteristic
		Isotropic characteristic (thermal expansion coefficient)	Small deformation after joined with a semiconductor
Switch Contact	Tungsten switch contact with a density of less than 99.5%	Isotropic characteristic (electric resistivity)	Stable electric characteristics
		Small number of pores	High wear resistance
Structural Member (for use in high-temperature environment)	Tungsten structural member with a density of less than 99.5%	Small number of pores	Low contamination
		High recrystallization temperature	High strength at elevated temperature No deformation at high temperatures

INDUSTRIAL APPLICABILITY

The production method of the present invention can be used for production of the following members or products formed of a tungsten-based sintered body.

1. A discharge lamp electrode
2. A sputtering target
3. A crucible

4. A radiation shielding member
5. A resistance welding electrode
6. A semiconductor element mounting substrate
7. A switch contact
8. A structural member (pipe-shaped member, block-shaped member, etc.)
9. A member for semiconductor manufacturing equipment
10. A member for an ion-implantation apparatus
11. An internal member for a nuclear fusion reactor